5-10-2017

ENERGY STORAGE IN LAYERED MoS2/ GRAPHENE COMPOSITE SUPERCAPACITOR DEVICES

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By

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Finishing B.S., Southern Illinois University-Carbondale, 2017

A Thesis submitted to the University Honors Program in partial fulfillment of the requirements for the Honors Diploma

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Southern Illinois University-Carbondale

May 10, 2017

AN ABSTRACT OF THE THESIS

John T. Barron, for the Honors Diploma.

TITLE: ENERGY STORAGE IN LAYERED MoS_2/GRAPHENE COMPOSITE SUPERCAPACITOR DEVICES

MAJOR PROFESSOR: Dr. Saikat Talapatra

Electrochemical Double Layer Capacitors (EDLCs), also known as supercapacitors or ultracapacitors, have gained much attention in the furthering of research into electronic devices and energy storage. Supercapacitors bridge the “gap” between conventional capacitors and batteries, and are of interest to furthering technology in alternative clean energy, transportation, and other areas of electronics. Nanomaterials are of interest in building these devices due to the presence of very high specific surface areas, unique electrical properties, and/or light-weight and flexible, but strong, structures. The goal of this project was to evaluate electrode materials for supercapacitor devices made from a composite of atomically thin layers of Graphene and Molybdenum Disulfide (MoS_2). Both materials were synthesized using a liquid phase exfoliation method via ultrasonication. The devices built with the composite materials (of varying concentrations) were tested using various electrochemical methods including cyclic voltammetry and galvanostatic charge-discharge to determine electrochemical properties and performance of the supercapacitors. The major motivation of this project was to optimize the concentration of MoS_2/Graphene composite electrode to which gives the top electrical performance as a supercapacitor electrode.

ACKNOWLEDGEMENTS

I would like to thank Dr. Saikat Talapatra for his guidance and aid both in the research that was necessary for this project as well as his guidance in making this thesis the best it can be.

I would like to especially thank graduate student Jacob Huffstuttler as well as undergraduate Julianna Richie for helping me to get started in research in Dr. Talaptra's lab and teaching me the fundamentals of the research covered in this paper. Without them, I doubt I would have been able to act as fluidly in the lab on research as I can today.

I would also like to thank undergraduate Sean Goff and graduate student Rana Alkhaldi for their aid in my research for this last semester.

I would like to thank the Center for Undergraduate Researcher and Creative Activities for awarding me the Research Rookies and REACH awards during my time as an undergraduate. These programs helped me to grow as a researcher and a student.

I would like to thank the Honors Program at SIU for their continued aid and encouragement in my education as well as in this paper.

Finally, I of course want to thank both my parents, James and Patricia Barron, for their encouragement in my education and life in general.

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INTRODUCTION

Technology is growing in favor of renewable, clean energy as well as smaller, more compact, and more durable devices. Fossil fuels are the main source of energy for most of the world today; however, this energy is non-renewable. To make matters worse, these fuel sources generally will pollute the atmosphere and contribute to global warming. In recent years, there has been extensive research into new technologies for collecting energy from clean, renewable sources such as wind and solar. In the area of energy storage for these technologies, a device with both high energy density as well as high power density would be ideal; however, such a perfect device does not exist. Capacitors have high power density (they charge and discharge fast), but they do not store enough energy to work as energy storage by themselves. Batteries have high energy density (they can store massive amounts of energy), but they are slow in delivery. For some technologies, large amounts of power need to be able to be delivered quickly. This is where supercapacitors come in. Supercapacitors are able to perform well in both energy density and power density, and can thus discharge and deliver a fair amount of energy fairly quickly. Supercapacitors are very popular in acting as "in-between" power sources for the short periods of time between when a system loses its primary source of power and when its back up battery/generator kicks into action. They have also seen use in the activation of emergency systems in doors of Airbus A380 airplanes, and have even been cited in use as the primary power source for public transportation which regularly visits charging stations[1]. At this point in time, supercapacitors perform somewhere between capacitors and

batteries as is apparent in **Figure 1**. The goal for future research and development will be to see if we (the scientific community) can further the performance of these devices so that they can outperform both devices in both energy and power density.

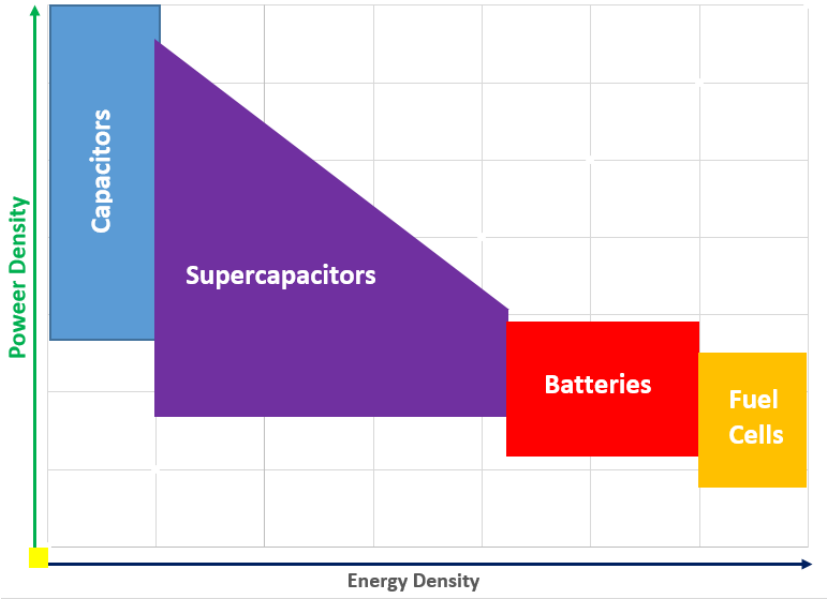

Figure 1: Simple model of a Ragone plot comparing power density and energy density for common energy storage device types

How a Supercapacitor Works

In order to aid in the production of these technologies, **E**lectrochemical **D**ouble **L**ayer **C**apacitors (aka Supercapacitors/Ultracapacitors) have become a focus of research in physics and material sciences. **EDLC**s are a wondrous energy storage device which features a greater energy density than your standard capacitor (more energy stored) as well as a greater power density than your standard battery (quicker energy delivery). The quick delivery of high energy makes these devices ideal for filling the gaps in alternative energy storage or turning on

backup/emergency items[1,2]. When built with lightweight nanomaterials, these devices allow for energy storage on a small scale with a longer life expectancy[2,3].

A traditional capacitor is formed by placing two conductive plates some distance from one another and adding a potential difference to the entire "device." The electrons will work against the electric field formed in order to move from the positive plate to the negative plate[4]. This movement of electrons will eventually result in the storage of charge between the two plates. The "capacitance" of the device is measured in farads and is described as the charge stored (coulomb) per potential difference (volts). The electric field can be reduced using a dielectric material to fill the space between the plates[4]. This will increase the capacitance of the device.

An EDLC is built by sandwiching a porous separator between two electrodes and immersing the entire device in an electrolyte. The electrolyte acts as the dielectric material in this case. The electrolyte allows for the ionic flow of charge between the electrodes through the porous separator, which keeps the device from discharging from electronic current[2]. The "double layer" is formed by the adsorption of ions onto the surface of the electrodes and the subsequent charge separation on each electrode from polarization[1]. Due to the presence of electrostatic storage, these electrodes do not suffer from redox reactions which increases the life expectancy of the device[1]. The double layer capacitance can be described by the following equation[1]:

$$C_{DL} = (\varepsilon_r \varepsilon_o A)/d \qquad (1)$$

In this equation, ε_r and ε_o represent the dielectric constants of the electrolyte and a vacuum, respectively, A is the surface area of the electrode, and d is the thickness of the double layer[1]. Conductive materials which feature a high specific surface area (with accessible pores) are ideal for making electrodes for the EDLC, as this will aid in the adsorption or ions and subsequently charge storage in the device.

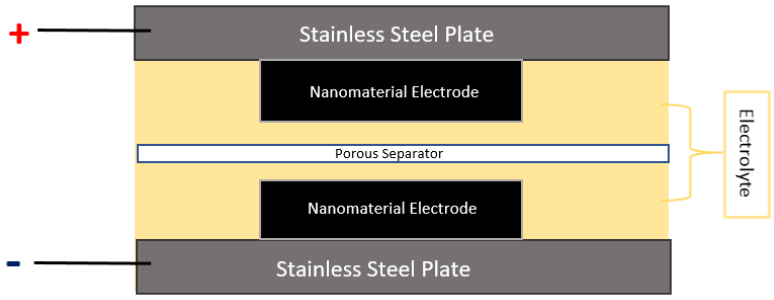

Figure 2: Simple outline for building an EDLC

Choosing the right electrolyte will also have a large impact on how well the device performs due to its place not only as the facilitator of ionic flow but also as the dielectric material for the capacitor. The stability of the electrolyte will also influence performance. The energy stored in a capacitor is proportional to the final potential squared[1,4]. Thus, increasing the voltage window on a device will exponentially increase the energy storage capabilities. Finding electrolytes which can sustain performance at higher voltage windows will fundamentally contribute to device performance.

Chapter 2

MATERIALS AND METHODS

Graphene

Graphene is an allotrope of carbon, which has monoatomic thickness and a hexagonal-basis honeycomb pattern. Graphene, unlike bulk graphite, is a highly conductive material. It also features high thermal conductivity, high mechanical strength, and large specific surface area[2]. This large specific surface area has been cited as theoretically being as high as 2500-2675 m^2/g [3,5,6]. Graphene's high specific surface area and conductive nature makes it an ideal material for building an EDLC.

Molybdenum Disulfide

Molybdenum Disulfide (MoS_2) is another interesting nanomaterial which features an indirect band-gap of 1.29 eV [7]. As MoS_2 transitions from bulk form to few layer or monolayer states, it also can undergo transitions from indirect to direct bandgap, sometimes acting metallically even[3,7]. Its indirect bandgap makes it a subject of study for photoluminescence and some study is also being done into how it adsorbs electrolyte ions[3,7]. MoS_2 is another good material for EDLC electrode fabrication, but its sometime semi-conductive properties can lead to increased resistance in the device as a whole.

Liquid Phase Exfoliation Method

Liquid phase exfoliation is one of the means by which researchers can mechanically turn bulk graphite and MoS_2 into few- or mono- layer nanomaterials. It has a few different

variations, but the one utilized here relies solely on the use of sonication and a well-chosen solvent. Sonic waves created in the solvent produce bubbles which burst into high-energy jets, breaking apart the material into nanoflakes[8]. The solvent, which has a high surface energy, prevents the agglomeration of the newly formed nanoflakes[8]. This method provides a simple, mechanical method to produce nanoflake samples for both materials listed above.

For synthesizing out materials, 0.5g of bulk MoS_2 powder was dispersed in 50mL Isopropyl Alcohol (IPA) (10mg/mL). This solution was subjected to horn-tip sonication for 4 hours at 25% amplitude. The sonicator used was a *Fisher Scientific Model 500 Sonic Dismembrator*. During sonication, the beaker containing the solution was placed inside a water and ice bath with a magnetic stirrer which was changed once every hour in order to ensure the solution did not experience any changes due to heat.

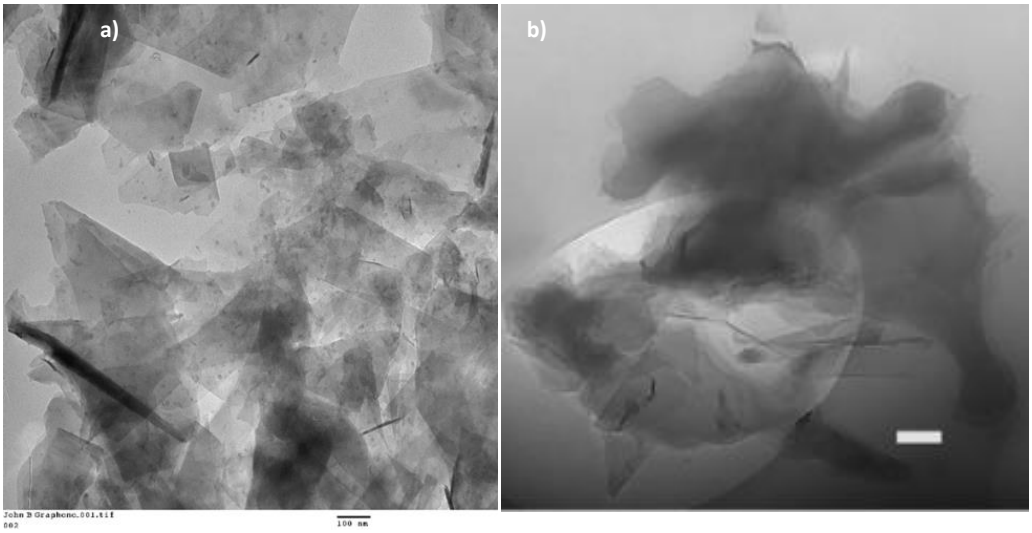

Figure 3: a) TEM image of LPE Graphene. **b)** TEM image of LPE MoS_2 [9]

0.5g of bulk graphite powder was dispersed in 50mL IPA (10mg/mL). This solution was subjected to bath sonication for 5 hours. The sonicator used was a *3510 Branson Bath Sonicator*

During sonication, the bath water was changed once every hour in order to ensure the solution did not experience any changes due to heat.

Following completion of sonication, each solution was centrifuged separately at 1500 rpm for 45 minutes (*Corning* Centrifuge). The supernatant fluid containing the nanoflakes for each was separated from the remaining bulk.

These solutions were vacuum-filtrated onto preweighed 0.1 µm Millipore filter papers and subsequently dried for 30 minutes at 50°C. Each filter paper had been weighed (alongside a blank) in order to determine the mass of remaining nanoflakes on the filter paper after drying. Prior to weighing, each filter paper (including the blank) was dried again for 10 minutes to remove any atmospheric vapor.

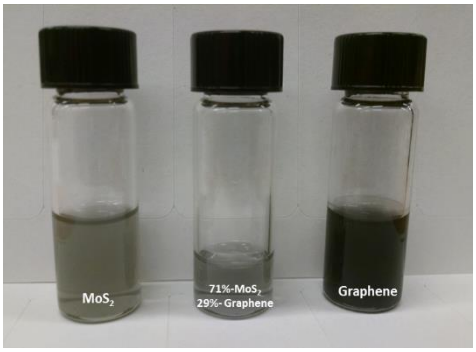

Figure 4: Collected liquid phase dispersions of MoS_2, Graphene, and the 71-29 MoS_2-Graphene composite.

Creating the Composite Electrode Materials and Supercapacitor Devices

Based on the mass of the MoS_2 and Graphene samples, the filter papers were each cut and divided into 1/8 pieces in order to give desired concentrations of MoS_2-Graphene. To make a composite solution, a number of portions were dispersed in 20mL IPA and bath-sonicated in 20 minute sets until the flakes were removed from the filter paper. The composite solution was then filtrated once again onto a new filter paper, dried, and weighed using similar methodology to the bulk materials.

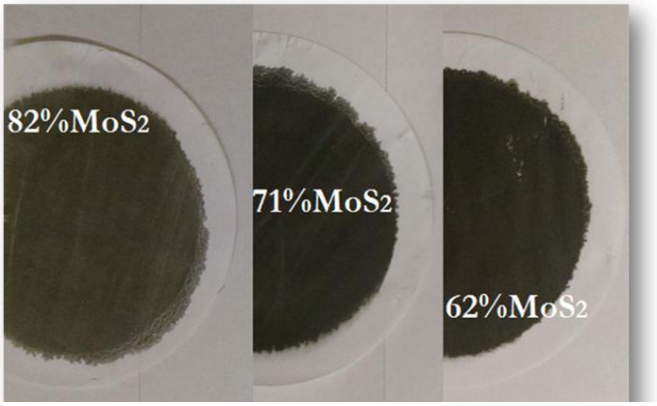

Figure 5: Vacuum-filtrated composite samples

To build a test device, small squares (≈2mm-5mm/side) of the desired composite of MoS_2-Graphene were cut and measured (the area of the device will be important in later calculations). These electrodes were then stacked with a porous filter paper in-between the electrodes to keep the device from discharging. The device was soaked in 6M potassium hydroxide (KOH) which acts as the electrolyte. KOH is an aqueous electrolyte with a voltage window of 1V. The test device was assembled inside of a *MTI Corporation Stainless Steel Split Test Cell* and attached to a *PARSTAT 2263* electrochemical analysis machine.

Electrochemical Experiments

Cyclic Voltammetry(CV), Galvanostatic Charge-Discharge(CD), and Nyquist measurements were made on each device. Cyclic Voltammetry is a measurement of current as the voltage is varied over a window. The voltage is scanned linearly for the anode and then again for the cathode, producing a "cycle" for the voltammetry study[10]. Cyclic Voltammetry was conducted on generally a 0.8V or 1V window (due to the voltage window of KOH) and varying scan rates from 1000mV/s to 10mV/s (sometimes measurements at 1mV/s were also taken). Charge-Discharge was run for 2000 cycles on a 0.1mA window in order to assess stability of the

device's performance and lifetime. Nyquist was run for Electrochemical Impendence Spectroscopy of the some of the devices with a frequency sweeping a range of 1MHz to 100mHz.

Data Analysis

The data which is considered in this thesis comes from three different sets of measurements made on composite devices as well as a set of data taken on electrodes made from just graphene. The concentrations for the composite devices is reported here as *%Concentration MoS_2 - %Concentration Graphene* (i.e. *71-29* would be 71% MoS_2 and 29% Graphene). Data Set 1 and Data Set 2 were measured in fall of 2014. Data Set 3 was measured in the spring of 2017 using newly synthesized Graphene and MoS_2. Data Set 4 consisted of solely a new device made from the 71-29 MoS_2-Graphene composite material from 2017. The data for the capacitive performance of each concentration was taken by analyzing the raw data from the CV curves. The values for capacitance were acquired by using the following equations:

$$C = \frac{\int I}{V \times \frac{dv}{dt}} \qquad (2)$$

$$C_{sp} = C/A \qquad (3)$$

$$C_{sp} = C/M \qquad (4)$$

All of the information needed for equation (2) could be acquired from our CV data. $\int I$ represents the integral of the CV curve (the raw data), V represents the voltage window for our scan, and dv/dt is the scan rate used. From there we could use equations (3) or (4) to acquire

the specific capacitance of the device. Equation (3) represents the specific capacitance by area of device, which is the raw capacitance value divided by the area of the smaller of the two electrodes (representing the plate area for the device). Equation (4) is the specific capacitance by mass, which is the raw capacitance divided by the calculated mass of the device. This mass value could be acquired by taking the mass of the total filter from which the electrodes were cut, dividing it by the area of the filter covered by material, and then multiplying it by the area of the smaller electrode times two (to account for the weight of both electrodes). Both equations (3) and (4) will be utilized by researchers today for reporting specific capacitance values and it generally varies from article to article which is used. For the purpose of this report, we will utilize equation (3), as when dealing with lightweight material, considering the capacitance with respect to mass in grams could increase the value of our specific capacitance more dramatically than is desirable for giving a precise report. Also, because determining the weight of the device considers other variables (measured weight of filter paper, size of each plate, assuming even spread of material on filter paper), using equation (3) instead of (4) gives less expected error.

Chapter 3

RESULTS

The devices built using composite materials generally outperformed those made from 100% MoS_2 or Graphene. This is apparent in **Figure 6**, as the area of the CV curve is directly proportional to capacitance. It is also apparent that there could be some disassociation of water molecules in the aqueous KOH electrolyte as the devices reach the 0.5V edges of the 1V window, as is apparent by the formation of curved peaks on each. In CV scans which were made in only the positive range (0-1V or 0-0.8V), this disassociation was even more apparent as the scan reached the far edges of the scan. This is important to consider as the peaks resulting from this disassociation will contribute to the capacitive behavior of the device but are not expected to be retained over time.

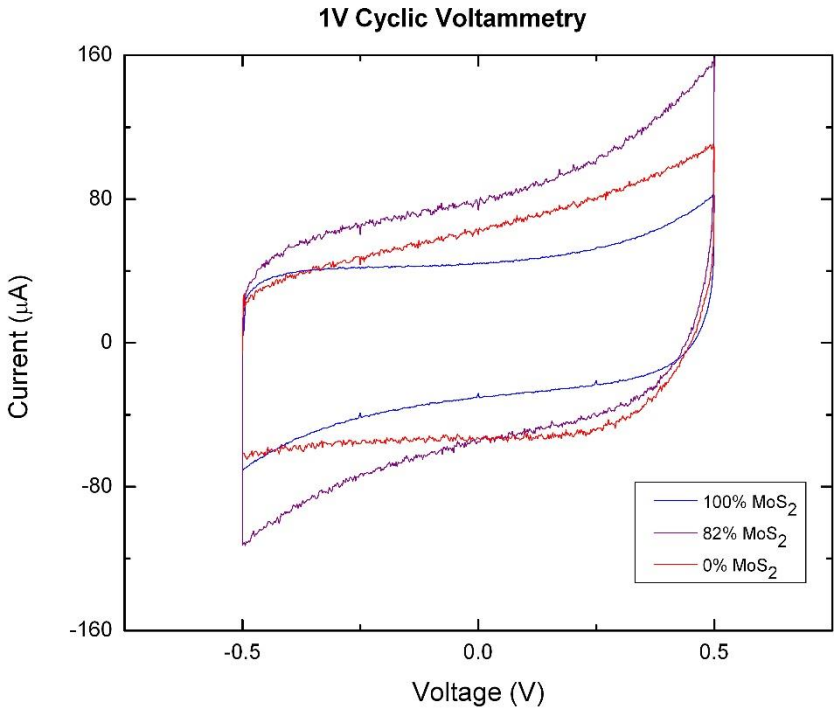

Figure 6: CV curves comparing MoS_2, the 82%-18% composite material, and Graphene

Figure 7 shows some of the last cycles for a CD curve taken on the 71-29 composite device. This figure shows that the composite device retains uniform performance after long periods of cycling. We hope to build more in the future on this analysis.

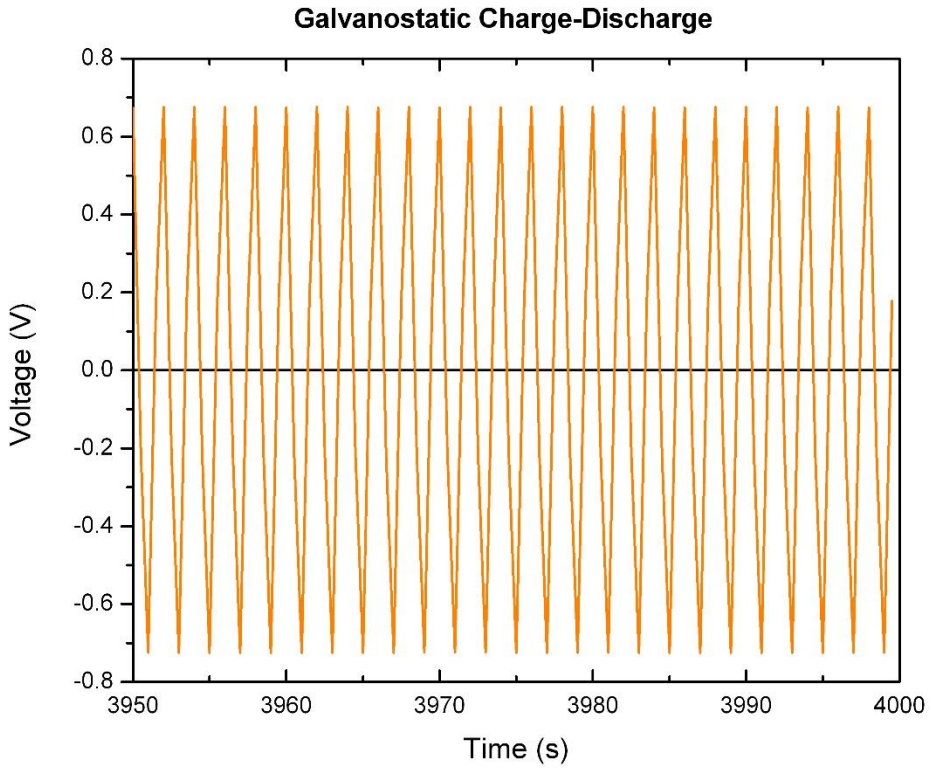

Figure 7: Charge-Discharge curve for 2000 cycles (1 second charge, 1 second discharge) of the 71%-29% composite device highlighting the last 25 cycles.

Data from CV curves were used in calculations to determine the capacitance values for each of the composite devices, and from there these values were normalized by area of the device to give the specific capacitance values (in mF/cm^2). **Figure 8** illustrates the comparison of these values to one another based on the concentration of MoS_2 present in the electrode material. The capacitance values for the CV curves at 10mV scan rate range from 0.79 mF/cm^2 to 2.57 mF/cm^2, which is comparable to similar composite devices being researched currently[3]. The specific capacitance at 10mV scan rate appears to peak around 70% MoS_2 with the values,

suggesting that this may be the optimal concentration of MoS_2-Graphene for supercapacitor electrode material. This concentration consistently gave the highest specific capacitance values for these composite samples

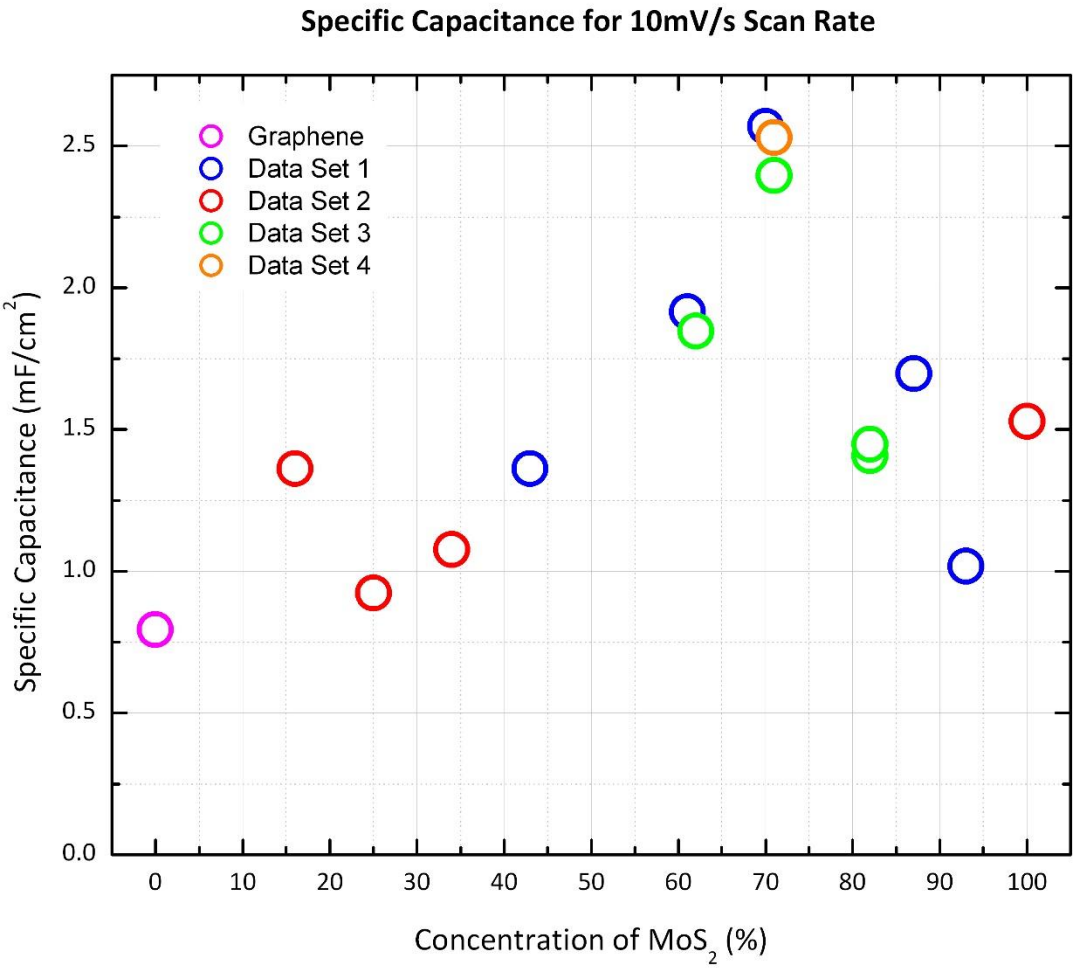

Figure 8: Specific Capacitance values for composite materials made with varying concentrations of MoS_2. Specific Capacitance was calculated by area.

Chapter 4

CONCLUDING REMARKS

Error Analysis

Possible sources of error in this study could include: possible human error in the handling/measurement of the filter paper samples during the construction of devices, possible mechanical error in the scale used to determine the weight of the samples, and chemical error in the possible disassociation of the KOH electrolyte during electrochemical testing. The first two are difficult to deal with beyond ensuring use of meticulous method, care, and measurement. For the third item, it was apparent from some study that the disassociation became more noticeable in the CV study as the voltage increased. This can be seen in **Figure 9**. Therefore, it is recommended that the voltage window used in CV be kept to <0.5V or that the window be studied on a -0.5V to 0.5V basis (1V window total). Another possible solution would be to switch to using an organic electrolyte with a larger voltage window of operation, such as BMP-FAP. This would also be of interest in general for the continued study of these materials. It is also worth mentioning that during the synthesis of new MoS_2 in the 2017 sample, the magnetic stirrer was forgotten in adding to the ice bath to maintain thermodynamic stability in the sonication. The ice bath was still changed every hour, so it is doubtful that this contributed to any degradation in the sample; however, this still could have been a source of error.

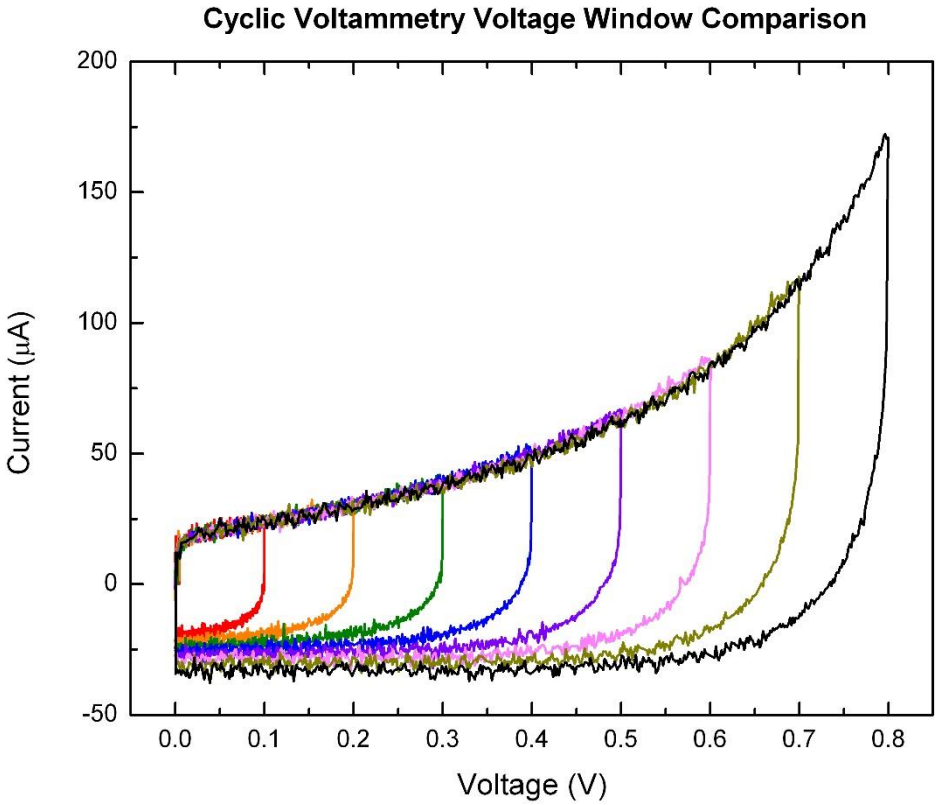

Figure 9: Cyclic voltammetry data for a 71-29 MoS_2-Graphene device, each with a varied scan window from 0.1-0.8V in the positive range.

Conclusion

The composite material of MoS_2-Graphene for electrodes proved to be excellent materials for building EDLC devices. The devices built showed strong lifetime and cyclability and greater electrochemical performance overall than the base materials. The high capacitance values we attribute partially to the possibility that 70%-30% MoS_2-Graphene could be an ideal concentration for minimizing ESR (resistance) in the material while still acquiring positive features of both base materials. Nyquist data is currently under investigation in order to decide the validity of this idea. Future recommended studies into this material would include repeated synthesis and characterization of new devices at different concentrations, TEM or SEM studies

into the stacking of the two nanomaterials in the composite form, and UV-Vis Spectroscopy on the composite solutions in order to determine the band gap created by the composition of these two materials.

Although further study is needed in order to improve our ideas of where the optimal concentration lies and why this is, from our data it seems undeniable that the mixture of few-layer MoS_2 and Graphene nanoflakes create a material which, as an electrode for EDLC devices, results in significantly increased capacitance. Understanding why this occurs will help the scientific community in its endeavors to improve EDLC-based technology and in the further research of materials science and electrochemistry in general.

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